

B. Engineered Surfaces for Diesel Engine Components

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Objective

- Evaluate new laser technologies such as surface dimpling, cleaning, and laser-assisted spraying to enhance adherence and increase coating strength.
- Develop phosphate-bonded composites for internal thermal management coatings.
- Evaluate new quasicrystalline materials as potential thermal barrier and wear coatings.

Approach

- Evaluate laser treatment techniques by treatment of small samples.
- Examine the resulting sample microstructures to determine the potential of the treatment method.
- Measure the mechanical and physical properties of phosphate-bonded composites and use them to determine their potential for use as thermal barrier coatings (TBCs).
- Evaluate the thermal stability of quasicrystalline materials using diffusion couples to assess the stability of the aluminum-based quasicrystalline materials at engine operating temperatures.

Accomplishments

- Completed cost analysis of laser pre- and post-treatments and selected post-laser “tacking” as the method for treating coatings to increase adherence.
- Developed phosphate-bonded composite coatings that survived initial thermal cycling to 650°C with good residual adherence to the substrate.
- Sprayed quasicrystalline coatings using the high-velocity oxygen fueled technique and began evaluating their thermal conductivities.

Future Direction

- Install a 2000-W Q-switched laser in Caterpillar’s thermal spray facility to investigate the effects of laser surface ablation on the adherence and density of thermal-sprayed coatings.

- Prepared phosphate-bonded coatings with high surface adherence that have shown promise as high-temperature adhesives as well as TBCs. Additional formulations are under development.
- Conduct additional oxidation studies as well as limited in-cylinder engine testing for the aluminum-based quasicrystalline coating, which has shown limited stability at 900°C in diffusion couples. At temperatures below 500°C, the material shows promise to retain the low thermal conductivity of the quasicrystalline state..

Introduction

Engine testing of thermal sprayed coatings has demonstrated their potential benefit as thermal barriers and as wear coatings to reduce fuel consumption, reduce wear, and reduce component temperatures.^{1,2,3} The durability of thermal sprayed coatings, particularly TBCs, remains the major technical challenge to their implementation in new engine designs. New approaches to coating design and fabrication will be developed to aid in overcoming this technical hurdle.

Three approaches to new TBCs have been pursued: (1) laser treatments applied to plasma-sprayed TBCs to modify their structures and adherence to enhance durability, (2) new quasicrystalline materials capable of being sprayed using a high-velocity oxygen-fuel (HVOF) process that produces denser coatings with higher bond strengths, and (3) new phosphate-bonded composites that allow for inner diameters to be coated and that have low thermal conductivity and high adherence.

Laser Treatments. Two types of laser treatments have been investigated. The laser-assisted plasma spray technique uses the power applied by the laser to completely melt the sprayed materials on the substrate to allow for metallurgical bonding and higher adherence of the coating. A second laser treatment, laser ablation, uses a high-power, short-pulsed laser to ablate the surface oxide on the substrate and interlayer of the sprayed material to increase the bonding of the coatings. Initial samples were produced using laser techniques that melted the sprayed materials to demonstrate the effect of the coating structure. Consultation with the Fraunhofer Institute in Dresden, Germany, provided sufficient confidence in the process to proceed with installation of a 4-kW YAG laser in Caterpillar's thermal spray laboratory for further process development. A review of the laser ablation technique with the University of Technology at Belfort-Montbéliard (UTBM) in France provided sufficient data to show that the technique has promise for improving the

adherence of sprayed coatings. Caterpillar is acquiring a Q-switched laser capable of producing the energy needed for the ablation process to proceed with this evaluation.

Quasicrystalline Materials. This new class of metallic materials exhibit low thermal conductivity with high thermal expansion as a result of their unique, aperiodic crystal structure. The material chosen for evaluation is an aluminum-based quasicrystal, $\text{Al}_{71}\text{Co}_{13}\text{Cr}_8\text{Fe}_8$, shown previously to be capable of 1100°C operation in a turbine engine.⁴ Initial diffusion couples have been run to aid understanding of the thermal stability of the alloy at operating temperatures.

Phosphate-bonded Composites. Phosphate-bonded composites consist of filler material bonded together by a phosphate. The compositions of both the filler and the phosphate binder can be widely varied and, for this reason, so can the properties of the composite. Phosphate-bonded composites are well known and have been in use for many years as refractory mortars and cements; high-temperature, corrosion-resistant coatings; temporary bone replacement; fast-cure paving cement; and dental cement.

Of the well-known phosphates, most are not suitable for high-temperature use. These include all of the hydrated crystal forms, such as those used for bio-replacement; low-temperature cements; and paving compounds, which simply decompose at elevated temperatures. Certain other non-hydrated alkali and alkaline phosphates are equally unsuitable because of their tendency to form low-melting-temperature eutectics in some environments. Metal phosphates have the highest potential for long-term chemical durability in high-temperature applications such as internal combustion and turbine engines.

Approach

Laser Treatments. Initial sprayed samples were treated using a key-hole laser beam to demonstrate the resulting coating structure. The samples were 10

mm in diameter with a substrate thickness of 3 mm. Coating thickness was approximately 0.5 mm with two types of coatings treated. One type of sample was the bond coating only with no ceramic top coat. The second coating type was a bi-layer bond coat/ceramic. The bond coating was a standard Ni-20%Cr-6%Al-0.5%Y, and the ceramic was 8% yttria-zirconia. The resulting laser-treated coating microstructures were analyzed for depth of penetration and cracking.

The laser ablation treatment was evaluated by reviewing the prior work preformed by UTBM in France. This work demonstrated good adherence for coatings applied to aluminum and titanium substrates. As these materials are highly reactive, the laser ablation done just prior to the coating application would remove the inherent surface oxide, allowing for better substrate wetting. Limited work has been done on steel and cast iron materials, but sufficient technical promise was shown for Caterpillar to invest in the Q-switch laser required for further process evaluation. The lasers will be delivered to Caterpillar in December 2004.

Quasicrystalline Materials. Owing to the metallic nature of the $\text{Al}_{71}\text{Co}_{13}\text{Cr}_8\text{Fe}_8$ quasicrystal, HVOF spraying techniques can be used to produce coatings with this material. The HVOF process produces higher density and better bonding of the coating than the plasma spray process by using high particle velocities at relatively low particle temperatures to “peen” or “forge” the particles onto the substrate surface. The low temperature of the process prevents ceramics from being sprayed using this technique.

HVOF coatings of $\text{Al}_{71}\text{Co}_{13}\text{Cr}_8\text{Fe}_8$ were produced for diffusion couple testing. Four diffusion couples were produced: (1) the quasicrystal and a steel substrate; (2) the quasicrystal, a Ni-17Cr-6Al-0.5Y bond coat, and a steel substrate; (3) the quasicrystal, a Ni-31Cr-11Al-0.6Y bond coat, and a steel substrate; and (4) the quasicrystal, a Fe-26Cr-8Al-0.4Y bond coat, and a steel substrate. The diffusion couples were produced by spraying a 12.5-mm-diam by 19-mm steel substrate with 0.5-mm-thick layers of the bond coatings and quasicrystal. The bond coatings were applied first, followed by the diffusion couple.

The diffusion experiments were conducted by sealing each type of sample in evacuated quartz tubes. Temperatures of 500, 700 and 900°C with

times of 25, 100 and 500 hours were used. The samples were water-quenched after annealing. Samples were then mounted and polished for examination by optical microscopy, scanning electron microscopy, and microprobe analysis.

Phosphate-bonded Composites. Research efforts on metal-phosphate composites at Caterpillar have been aimed at developing seal coatings, corrosion resistant coatings, and, more recently, thermal insulating coatings. Thin, corrosion-resistant coatings have been applied on various surfaces and have been successfully tested in various applications. Metal-phosphate adhesives have been used at Caterpillar for assembling prototype aftertreatment components for testing at temperatures around 800°C. Qualitative testing between phosphate-based and commercially available adhesives has shown the superior adhesive strength of the phosphate-based adhesives; however, quantitative characterization of the strength of phosphate-based adhesives was deemed necessary to assess their potential for high-temperature adhesive applications and as an intermediate step for the development of robust coatings.

Binder preparation and characterization. The basic stoichiometry of the phosphate material under consideration is $1.4 \text{ Al}_2\text{O}_3 \cdot 0.25 \text{ Cr}_2\text{O}_3 \cdot 3 \text{ P}_2\text{O}_5$. The binder preparation consists of continuously stirring orthophosphoric acid at 110°C and dissolving chromium trioxide, which is later reduced by adding sucrose; finally, alumina is added to the desired stoichiometry until it is fully dissolved. Additional chemistries, including the use of different chemical species and different proportions, are being explored.

Adhesive preparation and characterization. Adhesive composites consisting of 68% packed alumina with average particles of 0.7 μm were produced, filling the interstitial space with different phosphate binders. For lap shear testing, $1 \times 1 \times 0.5$ blocks of 90% pure alumina were used to make bonded, stepped specimens. The mixtures had a thick slurry consistency and were applied by brush on a section of the surface of the blocks. The brushed halves of two blocks were then aligned to form a step, obtaining a consistent alignment with an aluminum fixture that was built to produce five specimens at a time. Next, the fixture containing the samples was introduced to a curing oven at 300°C. A small amount of pressure perpendicular to the joint was applied at this stage.

Results

Laser Treatments. Laser tacking of the zirconia ceramic induces high amounts of cracking and void formation (Figure 1). Laser tacking of the bond coating material was more successful, in that cracking was suppressed during solidification of the material because of the higher ductility of the metal (Figure 2). This indicates that the laser-assisted plasma processing will need to be applied to thinner layers of the ceramic coating as it is built up during spraying to reduce the residual stress induced. Layer buildup during spraying usually proceeds at 0.025 mm or less for the ceramic layers. If the laser beam interaction time can be adjusted to provide sufficient heat input during coating application, it should be possible to build the ceramic layer without detrimental cracking.

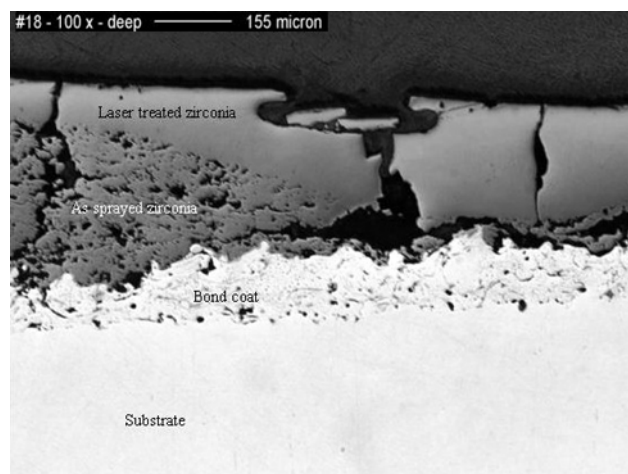


Figure 1. Laser tacked ceramic using medium laser power showing melting of the zirconia layer with crack and void formation.

Quasicrystalline Materials. HVOF spraying of the quasicrystalline material produced a dense, well-bonded structure (Figure 3). The stability of the quasicrystalline material at 700°C when in contact with the steel substrate material was fair, and a minor interaction zone was created after 500 hours (Figure 4). Cracking in the diffusion couple samples is due to the high stress state caused during water

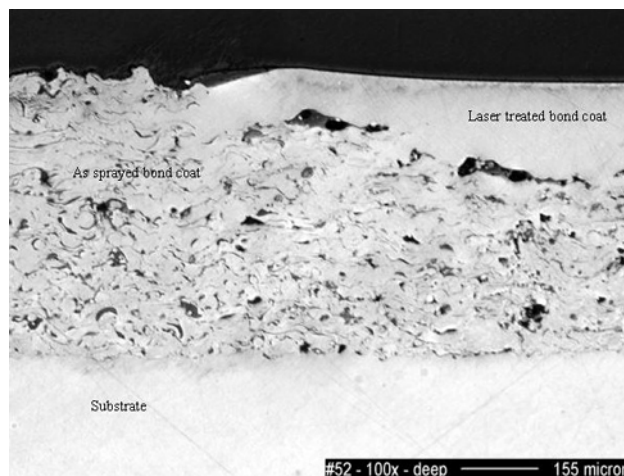


Figure 2. Laser tacked bond coating at medium laser power showing melting of the bond coat material with fusing into the coating and oxide formation under melt pool.

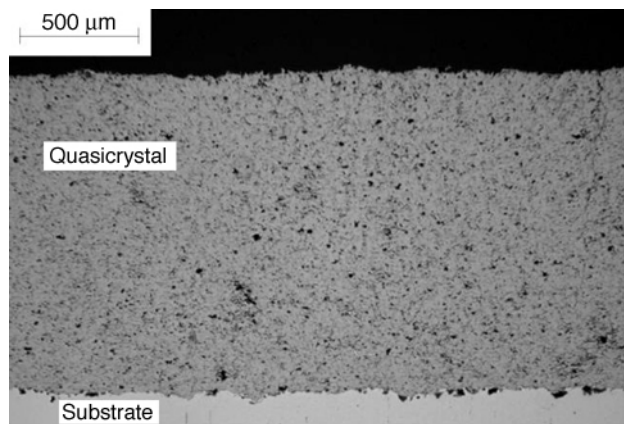


Figure 3. HVOF quasicrystalline material showing dense, well bonded coating structure.

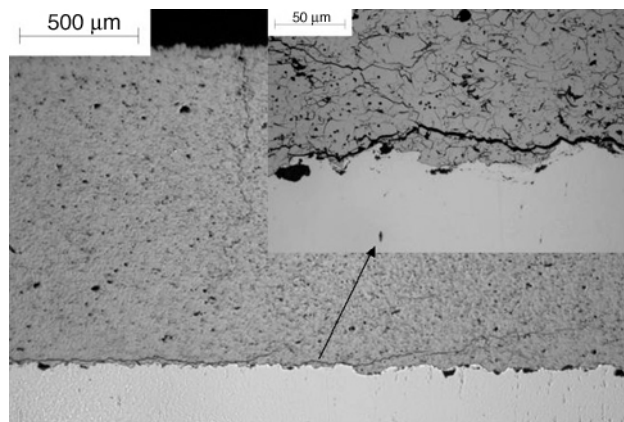


Figure 4. Quasicrystal/substrate diffusion couple after 500 hours at 700°C showing small reaction zone at interface.

quenching of the samples after exposure. At the higher 900°C temperature, the reaction zone with the substrate increased substantially, as expected (Figure 5). When coupled with the nickel-based bond coatings, large reaction zones were developed at the 700°C temperature (Figure 6), probably as a result of the higher reactivity of the aluminum with the nickel. As with the steel substrate, a smaller reaction zone was found with the iron-based bond coat (Figure 7). Microprobe analysis of the diffusion couple samples is under way to better understand the interaction of the materials at temperature. Oxidation samples will be made and exposed at similar temperatures to determine the effect of oxidation on the material stability.

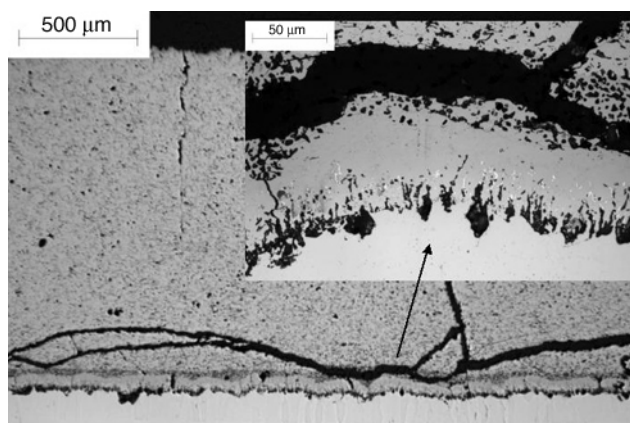


Figure 5. Quasicrystal/substrate diffusion couple after 25 hours at 900°C showing small reaction zone at interface.

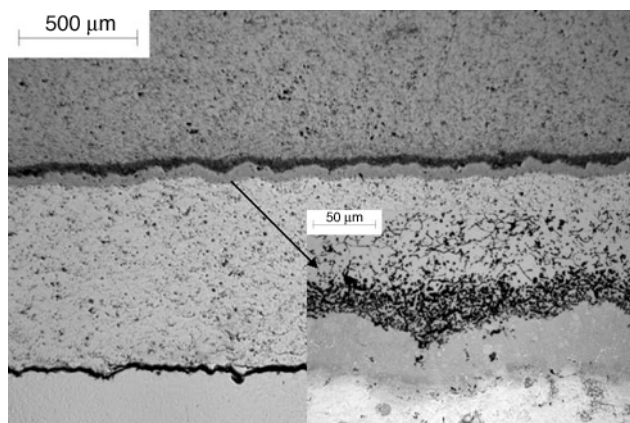


Figure 6. Quasicrystal Ni-31Cr-11Al-0.6Y diffusion couple after 500 hours at 700°C showing large reaction zone at interface.

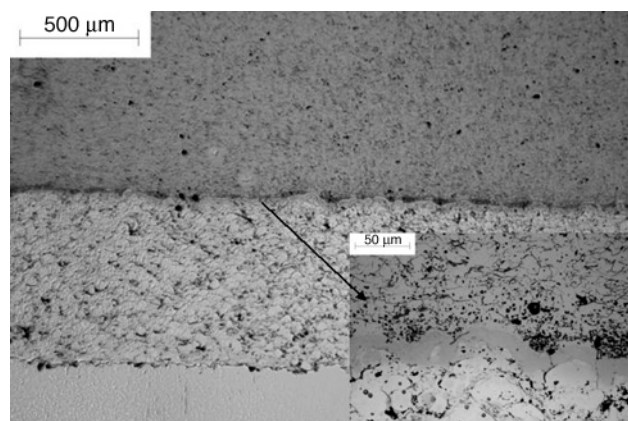


Figure 7 Quasicrystal/Fe-26Cr-8Al-0.4Y diffusion couple after 500 hours at 700°C showing a large reaction zone at interface.

Phosphate-bonded Composites. Evaluation of the shear strength of the different metal-phosphate-based adhesives and two commercial adhesives was conducted following the ASTM D401 standard. The fixture used for this test is shown in Figure 8.

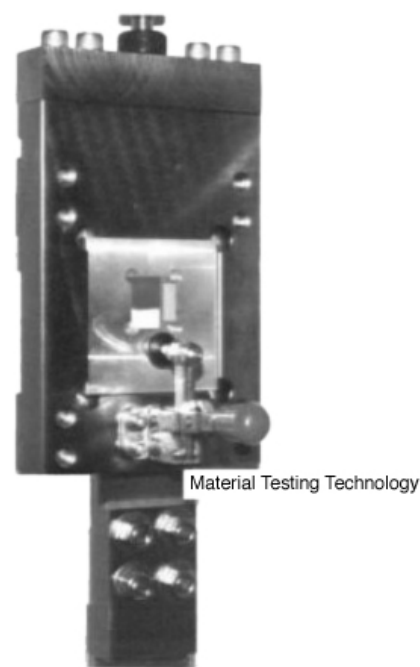


Figure 8. Fixture used for measuring the shear strength of the adhesives as per ASTM D401.

Data obtained from the shear lap testing are shown in Figure 9. Results are presented for the phosphate adhesive Ad7, which is the phosphate adhesive that yielded the highest strengths on the first round of experiments. Strength data of two

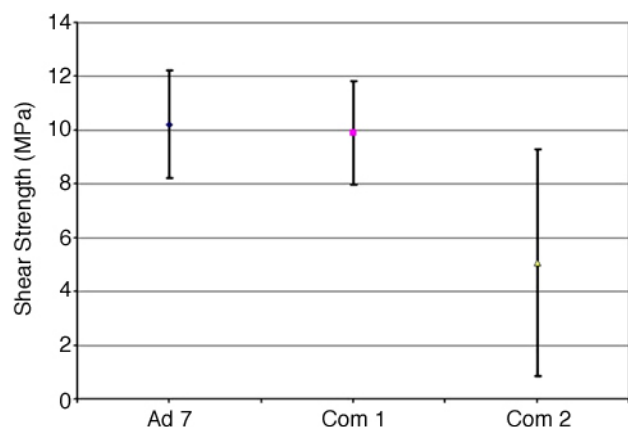


Figure 9. Measured strengths of adhesive produced in-house, Ad7, compared with commercially available adhesives Com-1, Com-2.

commercial adhesives, designated as Com1 and Com2, are shown for comparison. The error bars represent the standard deviation. These preliminary results suggest that phosphate adhesives can be produced with strengths of at least the same level as commercial adhesives. Testing with other phosphate formulations is continuing. Selected formulations showing the highest shear strengths will be used for continuing coating development.

Conclusions

Laser Treatments. Sufficient promise has been demonstrated for laser surface treatments to proceed with moving a 4-kW YAG laser into Caterpillar's thermal spray laboratory for further evaluation of the laser-assisted plasma spray process and to procure a Q-switched laser system for evaluation of the laser ablation method. Moving the YAG laser and procuring the Q-switched laser are being done independently of the current program funding.

Quasicrystalline Materials. The reaction zones of the substrate/quasicrystalline and Fe-26Cr-8Al-

0.4Y/quasicrystalline diffusion couple samples indicate some promise for limiting the interdiffusion of the materials in a TBC structure by designing the coatings to have interface temperatures of below 500°C. The ability to use a graded design may be limited by the reactivity of the quasicrystalline material with the bond coating materials used for grading. Further evaluation will be necessary to understand what types of graded designs can be made.

Phosphate-bonded Composites. The current phosphate-bonded composite shows much promise as a high-temperature adhesive, and commercialization of the material for this use will be pursued.

References

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